N64-29171
(ACCESSION NUMBER)
(THRU)
39
(PAGES)
1
(CODE)
Cr 56943
(NASA CR OR TMX OR AD NUMBER)
06
(CATEGORY)
FACILITY FORM 602

39p

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THE BORDEN CHEMICAL COMPANY

A Division of The Borden Company

GODFREY AVENUE AND LANGDON STREET

P. O. BOX 9524, PHILADELPHIA 24, PA.

SECOND QUARTERLY REPORT

To

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

Covering

RESEARCH AND DEVELOPMENT OF SEPARATORS FOR SILVER OXIDE-ZINC AND SILVER OXIDE-CADMIUM CELLS FOR SPACECRAFT APPLICATION

For the Period
September 27, 1963 - December 27, 1963

Contract No. NAS-5-3467

The Borden Chemical Company
Central Research Laboratory
Philadelphia, Pa. #19124

February 7, 1964

Written by H. E. Hoyt
H. E. Hoyt, Project Leader
Helmuth L. Pfluger
H. L. Pfluger
Laboratory Head - Polymerization

Approved by: Samuel Loshaek
Dr. Samuel Loshaek
Director of Research & Development
The Borden Chemical Company

PROJECT PERSONNEL

In carrying out the experimental work on this project at The Borden Chemical Company, the writers have been assisted by Dr. George Kitazawa, head of physical testing laboratory, and by Messrs. Richard Trickey and J. Kaczaj, and Gregory Cali and Harold Herring, assistants. In carrying out the sub-contract tests at Burgess Battery Company, Dr. Howard Strauss has the assistance of Messrs. Frederick A. Poss and Theodore A. Carus.

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I. INTRODUCTION

This is the second quarterly report covering work during the reporting period September 27, 1963 through December 27, 1963 on Contract No. NAS-5-3467 which was awarded to The Borden Chemical Company by the National Aeronautics and Space Administration, Goddard Space Flight Center, on June 27, 1963. The Burgess Battery Company of Freeport, Illinois, is participating in this contract in manufacturing and testing cells which incorporate separators developed for this study.

In the first quarterly report films were cast from a variety of polymer types and tested by bench scale procedures for suitability as membranes for silver-oxide-zinc cells. Films showing acceptable properties were prepared in quantity and forwarded to Burgess for accelerated life tests in cells. During the present period the same plan was followed, and elaborated with the objective of further elucidating the relationship of chemical structure to membrane performance in cells.

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II. SUMMARY

Polymers of a wide range of polarity were cast as films and screened as potential separators by tests for conductivity and solubility behavior.

Only water soluble polymers showed conductivity in 30% and 40% KOH of the order of cellophane. More narrowly, only those in this category which substantially absorbed the KOH solutions gave conductivity of the order of cellophane.

Several modifications of polymers have formed homogeneous films which have good conductive and tensile properties.

Resistance of films to oxidative action of silver oxide in KOH was studied. Irregular results have led to elaboration of this test for the purpose of achieving higher controls. These experiments are still in progress.

Several candidate membranes are being tested at Burgess Battery Company in cells. Results are preliminary.

Auth.

III. FUTURE PROGRAM

(1) Work toward improvement in the KOH-Ag_2O oxidation test should be continued.

(2) Conductivity measurements to date have been designed to give a preliminary rapid screening. Study of statistical variations is needed for precise work.

(3) Preparation of 8" x 40" films of modified methyl cellulose of enhanced conductivity is planned.

(4) Further work in preparing and modifying polyamine polymers is planned.

IV. WORK PLAN

The criteria for selecting candidates for testing in cells remain the same as outlined in the previous report. The separator should withstand strong alkali, be resistant to oxidation, have low electrical resistance, be an effective barrier to zinc, flexible, sealable and available in dry form.

V. EXPERIMENTAL SECTION

Some of the screening tests described earlier have been modified or elaborated as a result of experience in their use. These changes and new tests are described in principle below. Detailed descriptions will be given in the final report or on request.

Physical Tests - In the previous quarter the effects of oxidation by Ag_2O in KOH on the films, was preliminarily evaluated by a procedure in which the exposed films were removed from the solutions, blotted, conditioned at 50% R.H. and tested for flexibility in the Shopper Fold Tester. We now omit the conditioning step and test tensile strength directly after blotting. This is believed to approximate more closely the actual condition in which we are interested, namely the swollen film directly in the electrolyte environment. It would be desirable to have flexibility measurements also in this condition, but this is impossible with the Shopper Fold as presently designed. We have thus confined our physical testing to (a) the tensile strength of the virgin film at 50% R.H. and 73° F., (b) the strength after 72 hours soaking in 30% KOH, (c) the strength after 72 hours exposure to 30% KOH saturated with silver oxide. For (b) and (c) the tensile strips were removed from the liquids, the surfaces rapidly blotted dry and pulled in the Tinius Olsen Electromatic Universal Testing Machine. The elongation at break was recorded as a property correlating with the flexibility of the film in the electrolyte environment.

Electrolyte Absorption Tests - The weight of electrolyte absorbed and the consequent swelling are known to be related to conductivity and physical properties and are of practical importance in construction of compact cells. The term "absorption" as used in the reports under this Contract refers to the amount of electrolyte solution still remaining in the film after blotting with cellulose tissue paper. The films are soaked in the KOH solution, periodically removed, blotted and rapidly weighed. The process is repeated to constant weight. As a rule the most significant dimensional change was found to be in thickness and this change was observed by calipering the blotted films.

Conductivity - The conductivity cell pictured in the previous report was instrumented with a General Radio 650A impedance bridge and cathode ray oscilloscope to indicate null point. This provided measurements on the resistance of electrolyte plus membrane which suffice for a rough screening.

Film Casting - The procedure for the preparation of polymer solutions varies with the properties of each polymer. Solvents, concentrations, and doctor blade settings must be adjusted to obtain desirable viscosities for laydown and solids content for film thickness. Solutions were poured at such concentration and with such a clearance on the doctor blade as to give a dried film of 1 to 2 mils thickness. The surface was levelled plate glass in most cases, or where adhesion to glass was too great for removal of the dry film the plate glass was covered with a stretched film of polyethylene or Saran. Films were covered with glass baking dishes to inhibit initial evaporation.

In the preparation of larger 8" x 40" films for test cells the films after casting were covered with a wooden frame provided with a screen of finely woven percale and a removable second cover of polyethylene. The latter was used in those cases where it was desired to inhibit initial evaporation. The percale served to filter out dust particles. Solutions were pressure filtered or centrifuged to remove insoluble matter. Films were of good quality and uniform thickness.

For larger scale preparation commercial films were used, made to our specifications. These films are slightly oriented in the longitudinal direction. The effect of this on physical properties is under study.

Pinhole or Micropore Test - This is a qualitative test adapted from paper coating technology (TAPPI T54 M60) to show the presence of pinholes or micropores in the coating. A turpentine solution of a red dye is uniformly and sparingly distributed on the film surface by means of a mound of Ottowa sand. The presence of pinhole imperfections was revealed by the appearance of red spots on a piece of filter paper on the under side of the film. The film must of course be turpentine insoluble, which condition held for the water-soluble films of this study.

30% KOH Penetration - This test was developed by analogy to the above. A blue dye, sodium alizarin sulfonate, was dissolved in 30% KOH. The film under test was soaked in 30% KOH to equilibrium. The dyed KOH was then placed sparingly on a small heap of Ottowa sand on the upper surface and the appearance or non-appearance of the dye on the bottom side is noted.

VI. DISCUSSION

A. Solubility Properties

It was observed in our First Quarterly Report that only water-soluble or near water-soluble polymer types had thus far shown the order of conductivity of cellophane. The results to date, without exception, have been in agreement with this observation. A representative group of polymers illustrating the range of solubility encountered in the tests of this quarter is given in Table I. This is an extension of the work reported in Table II of the previous report. Some of the water-soluble polymers were soluble also in 30 and 40% KOH, therefore not useful directly as separator films. Two polymers, alginic acid and hydroxyethyl cellulose, showed borderline behavior, being soluble in 30% KOH, insoluble in 40% KOH.

Table I - Solubility Properties of Polymers

Polymer	Solubility in Water	Solubility in 30% KOH	Solubility in 40% KOH	Conductivity Level
Polyacrylic Acid	Sol	Sol	Sol	-
Polyethylenimine	Sol	Insol	Insol	Too soft to test
Polyacrylamid (A)	Sol	Sol	Sol	-
Poly(vinylmethyl ether)	Sol	Sol	Sol	-
Gantrez AN (B)	Sol	Sol	Sol	-
Hydroxyethylcellulose	Sol	Sol	Insol	High
Methyl cellulose	Sol	Insol	Insol	Intermediate
Poly (2 vinyl pyridine)	Swollen (14%)	Insol	Insol	Low
Poly (vinyl alcohol-formal) (C)	Swollen (197%)	Insol	Insol	Low
Polyethylene Oxide	Sol	Insol	Insol	Low
HEPVA-Modification A (ref. 407-27)	Sol	Insol	Insol	High
PVAlc-Modification C (ref. 407-28)	Sol	Insol	Insol	High
Methyl cellulose-Modification B (ref. 407-34-3)	Sol	Insol	Insol	High
Methyl cellulose-Modification A (ref. 407-34-1)	Sol	Insol	Insol	High

(A) Cyanamid Company.

(B) Copolymer of methyl vinyl ether and maleic anhydride.

(C) Experimental Copolymer (36.6% polyvinyl alcohol, 63.4% formal of polyvinyl alcohol).

Figures 1, 2, 3, 4 depict the absorption of electrolyte with time of the more important films studied this quarter. Most of these show a substantial degree of conductivity. (See below.) From the data it is possible to calculate the swelling which occurred in volumetric terms and to correlate this with the thickness increase (the principal dimension change). This is shown in Tables IIIa and IIIb. The agreement is good, considering the precision of both tests.

The data in Tables IV and V indicate that as electrolyte absorption decreases, conductivity also decreases. Such a correlation of swelling with electrical conductivity has been noted by earlier workers. The case of polyethylene oxide films in this study is instructive (Table V). Early films (389-61-HE) appeared to be an exception to the relationship in that they did not measurably absorb electrolyte, yet were found to be conductive. However, microscopic and electron microscopic studies (Fig. 5) showed what appeared to be relatively bulky crystalline masses bound together by a very thin film matrix. This matrix was readily ruptured in the electron beam. Pinholes or micropores were suspected from this as well as from the discontinuities visible to the naked eye in stretched film. This appeared to be confirmed by the TAPPI turpentine penetration test (Table VII). When improved films were made by double layer coating and hot casting on hot plates (which partially dissolved some of the haze, that is, crystalline aggregates) penetration and conductivity were simultaneously reduced. If completely flawless films could be produced it is our opinion that conductivity figures would be of the order of completely non-conductive films.

Methyl cellulose also illustrates the relationship of electrolyte absorption and conductivity (Table IV and Figs. 1, and 2). Here a material of intermediate conductivity shows only moderate absorption of 30% and 40% KOH.

Table VII summarizes TAPPI turpentine-dye tests on a number of polymers. The original use made of this test was to reveal suspected discontinuities in polyethylene oxide films. It was also applied to the Gelman membranes in Table VI which also showed penetration. These are polymer-impregnated nylon cloth. Other membranes were included in the table primarily as controls.

The tests of Table VII leave unanswered the question of whether the electrolyte-swollen membranes are permeable. To answer this an analogous test was devised (Table VIII) in which the membrane was equilibrated with 30% KOH by soaking overnight, blotted, placed over a piece of filter paper, covered with a small heap of sand, 30% KOH containing a blue dye added in an amount just to wet the sand, and the assembly covered to limit evaporation. Penetration to the reverse side occurred rather quickly with conductive films; there was no penetration with poor conductors. The methyl cellulose films (of intermediate conductivity) showed no penetration in the test.

B. Chemical Resistance of Films

To simulate cell environment films of various chemical types were exposed to 30% KOH in the presence of Ag_2O, continuously stirred to assure solution. Visually, it was readily apparent that the films most quickly and completely attacked were those which absorbed KOH and which were conductive. Poorly conductive films such as the acetals of polyvinyl alcohol, ethyl cellulose, poly-2-vinyl pyridine and Methocel HG were markedly more resistant.

In order to more quantitatively evaluate the oxidation effect the films were removed from the oxidation bath, blotted dry and immediately tested for tensile and elongation. A considerable body of data is at hand on the loss in tensile by this treatment. Although good reproducibility was found on replicate tests the variation from one set of tests to another has been inordinate in the case of conductive films. Thus, on the same lot of PUDO cellophane 193, tensile after 72 hours exposure to the oxidation test have varied from zero (almost complete disintegration) to 4378 psi. It is possible that the silver mirror formed on the surface of the specimens varies in permeability. However, the reasons for the irregularities are not obvious at this time and further work on the method is required.

In Table X the tensile data on the original strips, conditioned at 50% R.H. and after exposure to 30% KOH (only) are given. The latter shows the effect of 30% KOH (chiefly plasticizing) on the physical properties and will serve as control values on oxidation tests when the method is improved.

C. Polymer Mixtures in Films

The non-uniformity of polyethylene oxide films led to an attempt to plasticize the apparently crystalline regions by addition of water-soluble polymers. It is interesting to note that in many cases two water-soluble polymers formed two phase systems as shown in Table IX. Films from such systems consisted of globules of one polymer dispersed in the other and were not further tested.

D. Polyacids and Polybases

Most of the candidate polymers of our study owe their polarity and conductivity to hydroxyl or ether groups or both. It is well known that such structures lend themselves or adjacent groups to oxidation and it would therefore be of interest to study polymers whose polarity derives from groups more stable to oxidation. In this category we have considered polyacids (which are too soluble in unmodified form) and polyamines. Polyethylenimine from two commercial sources proved to be insoluble in 30% KOH but the film was too soft for use. Chemical modifications to raise the softening point are under study. Poly-(2-vinyl pyridine) was prepared by suspension polymerization. Unreacted monomer was removed by steam distillation. The gummy product was washed with water by decantation, and taken up in methanol. Films were cast from the methanol solution. Adhesion of these films to glass (with and without parting agents) and to chrome plate was so strong that it was not possible to remove them. Removal was possible by casting on polyethylene or Saran although some beading (cohesive action) defects occurred in the case of polyethylene. Films were relatively brittle in dry air but quite flexible in electrolyte.

The polymer was soluble only in highly polar solvents (insoluble in acetone) and was swollen 13% by water to give a highly extensible film, but gave no weight pick up in 30% and 40% KOH. Conductivity (Table V) was poor.

E. HEPVA Films

Three HEPVA films are under test at Burgess; all produced on commercial scale. The following table summarizes the preparative history and properties.

Table II - Properties of HEPVA Films

Number		374-59	374-60	79
Mol. Wt.		High	Med.	-
CRL Saponifiables	meq/g.	.07	.00	1.60
CRL free acid	meq/g.	.30	.05	.05
Hydrolysis of PVAlc	%	100	100	88
Percent ethoxylated		25-30	20-25	-
Wetting agent		trace (1)	trace (1)	-
Bleaching agent		trace (2)	trace (2)	-
Plasticizer		0	0	-
Water solubility after exposed to KOH		soluble	soluble	insol.
Appearance		clear and smooth	clear and smooth	sl. wrinkled

(1) Ethoxylated amine type
(2) Sodium metabisulfite

F. Hydrolyzed Formvar 7/70

This polymer, containing hydroxyl, acetate and formal linkages was hydrolyzed with excess alkali which attacks only the acetate groups, converting them to hydroxyl. The reaction was followed analytically and the polymer was converted from the composition at the left to that given on the right.

	Formvar 7/70 Original (Shawinigan Analysis)	Alkali-Hydrolyzed Formvar 7/70 (calcd. from NaOH consumed)
OH (as polyvinyl alcohol	5%	36.6%
Formal (as polyvinyl formal)	55%	63.4%
Acetate (as polyvinyl acetate)	45%	0%
30% KOH abs. % orig. wt.	102%	107%
Water Abs. % orig. wt.	105%	197%
Conduct. 30% KOH mhos/cm	9.4×10^{-4}	4.7×10^{-3}

Neither the original nor saponified product gave the required conductivity. The film from the hydrolyzed product was not dissolved in water but was plasticized to an almost liquid state. However, it did not pick up sufficient electrolyte from our concentrated KOH to give the required level of conductivity.

G. Development of Separator Test Systems at Burgess

Preliminary tests on single cells were run at Burgess with design parameters as summarized in Tables XI and XII. Dupont 193 PUDO cellophane was used to establish a level of performance. Because the PVAlc and HEPVA films were respectively three and two times as thick as the cellophane, correspondingly fewer layers could be used per plate side. The results of these single tests are interpreted by Burgess as follows. The high rate discharge performance of the cell with PVAlc was poor, however life cycle performance approached that of the cell containing cellophane. The cell with HEPVA performed quite favorably on high rate discharge and on life cycle test but failed abruptly on the ninth cycle due to shorting.

Detailed cycling data are brought together in Table XIII. Typical discharge voltage curves are shown in Figures 6, 8 and 10. Discharge capacity as a function of cycle number is plotted in Figures 7, 9 and 11.

Repeated tests are necessary to establish variance of performance and to compare the mean performances of each type of diaphragm. Additional cells with Borden HEPVA 79 are being constructed at Burgess and will be cycled. Two other commercial films made from HEPVA of high (374-59) and medium (374-60) molecular weight respectively will also be tested in cells. Also submitted for cycle tests are two new PVAlc membranes 374-61 and 389-110, a methyl cellulose membrane 389-104 and a hydroxyethylcellulose membrane 389-121.

Table IIIa- Swelling in Electrolytes. Calculations

Membrane	KOH Conc. %	Orig. Wt. g.	Final Wt. 24 hrs. g.	Calcd. Final Vol. % of orig.(*)	Thickness Orig. mils	Thickness Final mils	Thickness Final % of orig.
Avisco Cellophane	30	.1155	.3141	234	1.2	3.0	250
	40	.1140	.2933	208	1.2	2.8	233
HEPVA 374-59	30	.1548	.2419	143	1.8	2.5	139
	40	.1556	.2439	141	1.8	2.3	128
HEPVA 374-60	30	.1370	.2263	150	1.5	2.2	147
	40	.1440	.2495	152	1.5	2.4	160
PVAlc 374-61	30	.1269	.2306	163	1.5	2.3	153
	40	.1274	.2685	179	1.5	2.4	160
PVAlc-Modification A(389-91)	30	.0812	.1823	196	1.3	2.3	177
	40	.0986	.2518	211	1.4	2.3	164
PVAlc-Modification C(407-28)	30	.0718	.1385	171	1.0	1.8	180
	40	.0738	.1788	201	1.0	2.2	220
HEPVA-Modification A(407-27)	30	.1046	-	-	1.1	2.4	218
	40	.1127	.4146	221	1.1	2.4	218
Formvar 7/70 374-41	30	.0621	.0636	102	0.9	1.0	111
	40	.0717	.0740	102	1.0	1.1	110
Hydr. Formvar 389-83	30	.0579	.0620	106	0.8	0.9	112
	40	.0658	.0686	103	0.9	0.9	100
Methocel 15 389-105 (a)	30	.1580	.1759	109	2.0	-	-
	40	.0945	.1125	114	1.5	1.6	107
Methocel 100 389-104 (a)	30	.0768	.0854	109	1.3	1.6	123
	40	.0724	.0859	114	1.3	1.5	116
Methocel 400 389-103 (a)	30	.0953	.1077	110	1.8	2.0	111
	40	.1010	.1227	115	1.6	2.0	125
Poly 2-vinyl Pyridine 389-101	30	.1166	.1132	100	1.6	1.8	112
	40	.1235	.1236	106	1.6	1.7	106
Hydroxyethyl Cellulose 407-26-1	30	- Soluble -		-	-	-	-
	40	.1075	.1764	146	1.4	2.4	171
H.E. Cellulose 407-26-2	30	- Soluble -		-	-	-	-
	40	.0983	.1620	149	1.4	2.2	157
H.E. Cellulose 407-26-3	30	- Soluble -		-	-	-	-
	40	.1496	.2764	163	1.7	2.9	170

Note* Volume changes are calculated from weight changes and density of KOH solutions
(a) Methocel is a Dow trade name for Methyl Cellulose

Table IIIb- Swelling in Electrolytes, Calculations.

Membrane	KOH Conc.	Orig. Wt. g.	Final Wt. g. 48 hrs.	Calcd.* Final Vol. % of Orig.	Thickness Orig. mils	Thickness 48 hrs. mils	Thickness Orig %
HEPVA 79	30%	.2864	.4232	137	1.5	2.4	160
	40%	.2891	.5200	157	1.5	2.5	167
PVAlc 389-62	30%	.2110	.4006	170	1.6	3.2	200
	40%	.2067	.4939	199	1.6	3.5	218
Cellophane PUDO	30%	.1507	.4800	269	1.0	3.2	320
	40%	.1519	.4492	240	1.0	2.9	290
Methyl Cellulose 389-63	30%	.1775	.2248	121	1.5	2.1	140
	40%	.1852	.2339	119	1.5	2.1	140
Methocel HG (a) 389-44	30%	.0877	.0973	109	1.1	1.1	100
	40%	.0920	.0961	104	1.1	1.1	100
Formvar 15/95E 389-25	30%	.1146	.1136	100	1.2	1.4	117
	40%	.1084	.1084	100	1.2	1.3	108
Butvar B73 389-23-2	30%	.1194	.1194	100	1.5	1.3	87
	40%	.1275	.1275	100	1.5	1.5	100
Polyox H 80 389-61-HE-2	30%	.3156	.3172	100	3.0	3.2	107
	40%	.3133	.3178	100	3.0	3.1	103
Ethocel T 100 389-49-1	30%	.1406	.1401	100	1.4	1.4	100
	40%	.0939	.0934	100	1.4	1.4	100
Ethocel G 100 389-49-2	30%	.1459	.1468	100	1.5	1.5	100
	40%	.1540	.1465	96	1.5	1.5	100

* Volume changes calculated from weight changes, assuming KOH and water are absorbed in proportion to their concentration in solution.

(a) Dow grade of modified methyl cellulose.

Table IV - Electrical Conductivity and Electrolyte Absorption at Equilibrium Present Candidates

Notebook Reference	Composition	30% mhos/ cm	KOH Wt. % of Orig.	mhos/ cm	40% KOH Wt.% of orig.
PT 191 (A)	No Membrane	.52	-	.46	-
374-30	Cellophane PUDO 193	.52	318	.46	295
374-42	Cellophane Avisco 150 PI	.51	272	.46	251
79	HEPVA (Hydroxyethylpolyvinyl alcohol (B)	.53	148	.46	180
374-59	HEPVA (high mol. wt.)	.59	156	.50	157
374-60	HEPVA (med. mol. wt.)	.59	165	.46	173
407-15-3	HEPVA (2913 Leomflex Lot 4082) (C)	.60	-	.52	-
374-61	PVAlc (Unplast., commercial)	.58	163	.50	179
78	PVAlc (commercial) (B)	.52	-	.10	-
389-37	PVAlc (D)	.46	190	.44	220
389-106-1	PVAlc (D)	.54	189	.50	180
389-63	Methyl Cellulose (15 cps. C.P.)	.31	113	.044	113
389-105	Methyl Cellulose (Methocel 15)	.32	111	.030	119
389-104	Methyl Cellulose (Methocel 100)	.31	111	.08	119
389-103	Methyl Cellulose (Methocel 400)	.38	113	.12	121
407-34-2	Methyl Cellulose Modification A	.48	-	.15	-
407-34-3	Methyl Cellulose Modification B	.50	-	.29	-
407-34-4	Methyl Cellulose Modification C	.48	-	.24	-
407-26	Hydroxyethyl Cellulose		Soluble	.51	165
389-91	PVAlc Modification A	.59	195	.50	243
389-92	PVAlc Modification B	.60	-	.50	-
407-28	PVAlc Modification C	.57	178	.40	239
407-27	HEPVA Modification A	.60	256	.50	368

Notes

(A) This should be the base line and maximum conductivity possible. However instrument reading at null point was occasionally higher than this on conductive films.

(B) Membranes tested at Burgess, this report

(C) Borden HEPVA made from 30-98 PVAlc, 25% ethoxylation.

(D) Unplasticized PVAlc 30-98.

Table V. - Electrical Conductivity and Electrolyte Absorption of Films
Rejected Candidates

Reference	Composition	30% KOH Mhos/cm	30% KOH Wt. % of Orig.	40% KOH Mhos/cm	40% KOH Wt. % of Orig.
374-41	Copolymer Formvar 7/70 (A)	9.4×10^{-4}	102.3	2.1×10^{-3}	103
398-83	Copolymer Hydrolyzed Formvar 7/70 (B)	4.8×10^{-3}	10.7	9.6×10^{-4}	104
389-61-35	Polyethylene oxide (Polyox 35) (C)	7.7×10^{-2}	-	8.9×10^{-2}	-
389-61-HE 1	Polyethylene oxide (Polyox 80) (D)	.41	100	.38	101
407-12	Polyethylene oxide (Polyox 80) (E)	2.7×10^{-3}	102.7	6.6×10^{-3}	99
407-13	Polyethylene oxide (Polyox 80) (E)	7.8×10^{-4}	100.5	6.7×10^{-4}	101
407-14	Polyethylene oxide (Polyox 80) (E)	2.9×10^{-3}	-	3.8×10^{-3}	-
389-101	Poly(2-vinyl pyridine) (F)	16.2×10^{-6}	103	1.9×10^{-4}	100
389-49-1	Ethyl Cellulose (Ethocel T100) (G)	4.6×10^{-5}	100	16×10^{-5}	100
389-49-2	Ethyl Cellulose (Ethocel G100) (G)	6.5×10^{-5}	101	2.4×10^{-5}	100
374-41	Silvered Formvar 7/70 (H)	1.7×10^{-3}	-	6.1×10^{-4}	-
389-88	Copolymer (RHOPLEX) (I)	5.4×10^{-5}	-	-	-
	Polyethylenimine (Borden Monomer-Polymer)	too soft to test - insol. KOH			
	Poly(vinyl methyl ether-maleic anhydride) (K)	soluble, brittle film			
	Poly(methylvinyl ether)(L)(\)	too soft to test, insol KOH			
	Polyacrylamid (Cyanamer P25, P26) (N)	soluble, brittle, unstable.			
Blends of Polyox 80 and Gantrez AN 119					
374-39	8/20 (Films were clear	.54		.43	
389-77	82/18 but brittle	.52		-	
389-76	73/27 and weak)	.51		-	
389-79	50/50	Sol		Sol	

Notes for this table on following sheet.

Table V. - Notes:

(A) Shawinigan. A formal of incompletely hydrolyzed polyvinyl alcohol: 5% polyvinyl alcohol, 55% polyvinyl formal, 45% polyvinyl acetate.
(B) Saponified product of the above 36.6% polyvinyl alcohol, 63.4% polyvinyl formal.
(C) Union Carbide.
(D) Union Carbide. Film was microporous, imperfect.
(E) Improved films by double coating and heating.
(F) Synthesized for this project.
(G) Hercules.
(H) Film after oxidation by silver oxide in KOH.
(I) Rohm & Haas Copolymer.
(J) Union Carbide.
(K) General Anilin, Gantrez AN 119.
(L)(M) General Aniline, Gantrez M155, M555.
(N) American Cyanamid.

Table VI. - Electrical Conductivity of Commercial Membranes

Name	Company	Probable Composition	Conductivity 30% KOH Mhos/cm
Cellophane	Du Pont	Unplasticized PUDO	.53
Cellophane	Visking	Avisco	.51
Polypor WA	Gelman	Weak polyacid dispersed in Dynel supported by Nylon cloth	.575
Polypor WM	Gelman	Weak basic ion exchange (polyamine) dispersed in Dynel supported by Nylon cloth	.153
Millipore OS	Millipore	"Solvent resistant 3-10 microns"	12.9×10^{-5}
Millipore OH	Millipore	"Solvent resistant 0.5 to 1.5 microns"	5.2 x 10

Note: The Polypor membranes were permeable to TAPPI test, indicating micropores. Conductivity may be due to these openings.

Table VII - Penetration of Dry Films by Dyed Turpentine (TAPPI T454-M60)

Reference	Polymer	Penetration 1 hr.	Penetration 2 hrs.	Penetration 1 day	Conductivity mhos/cm. 30%KOH	Conductivity mhos/cm. 40%KOH
389-61-HE	Polyox 80 (A)	(15 min.)	yes	yes	.41	.38
407-14	Polyox 80 (B)	no	yes	yes	.018	.016
407-12	Polyox 80 (C)	no	slight	yes		
79	HEPVA	no	no	no	.53	.46
389-106	PVAlc	no	no	no	.54	.50
389-93	PVAlc	no	no	no	.46	.44
389-12	Cellophane	no	no	no	.53	.46
389-63	Methyl Cellulose	no	no	no	.31	.04
389-105	Methocel 15 (D)	no	no	no	.32	.03
389-103	Methocel 400 (D)	no	no	no	.38	.12
389-26	Butvar (E)	no	no	no		
374-41	Formvar 7/70 (F)	no	no	no		
389-49-1	Ethyl Cellulose		Dissolved film			
389-49-2	Ethyl Cellulose		Dissolved film			

Notes: (A) Cold cast, single film
(B) Hot cast film, improved homogeneity over A
(C) Double layer film, improved homogeneity over A
(D) Methyl cellulose
(E) Polyvinyl butyral
(F) Polyvinyl formal-acetate

Table VIII. – Penetration of 30% KOH-Equilibrated Films by 30% KOH
vs. Conductivity

Polymer	Passage of Dye			Conductivity	
	1 hr.	2 hr.	1 day	30% KOH mhos/cm	40% KOH mhos/cm
LEMOFLEX 79	spots	spots	spots	.53	.46
Cellophane PUDO	spots	spots	spots	.53	.46
PVAlc 389-93	"	"	"		
389-106	"	"	"		
389-62	no	no	spots	.46	.44
Methyl Cellulose 15	no	no	no	.31	.04
Methocel 100	no	no	no	.31	.03
Methocel 400	no	no	no	.38	.12
Methocel HG 30	no	no	no	1.5×10^{-2}	2.3×10^{-4}
Formvar 7/70	no	no	no	9.4×10^{-4}	4.4 x 10[illegible]
Butvar 80	no	no	no	6.2×10^{-5}	2.5×10^{-4}
Ethyl Cellulose T100	no	no	no	4.6×10^{-5}	1.6 x 10[illegible]
Ethyl Cellulose G100	no	no	no	6.5×10^{-5}	2.4×10^{-4}

Table IX. - Combinations of Water-Soluble Polymers

Reference	Combination		Parts		Result
389-89	Polyethylene oxide	1	PVAlc	9	Two layers
389-90	Polyethylene oxide	5	"	5	Two layers
407-8	"	5	HEPVA	5	Two layers (2)
407-31	"	5.5	Polyacrylic Acid	4.5	Two layers, bottom layer plastic
389-79	"	5	Gantrez AN*	5	Soft film, sol. in 30% KOH
389-98	Methylcellulose	5	PVAlc	5	Two layers
389-99	"	5	HEPVA	5	Two layers

*Gantrez AN = copolymer vinyl methyl ether and maleic anhydride.

(2) Bottom layer chiefly HEPVA by IR spectra.

Table X - Tensile Strength of Films at 50% R.H. vs. Saturation with 30% KOH

Reference	Description	At 73°C., 50% R.H. Tensile psi	At 73°C., 50% R.H. Elongation %	Soak 72 hrs. 30% KOH Tensile psi	Soak 72 hrs. 30% KOH Elongation %
379-30-1	Cellophane PUDO 193	17,200	32	4,700	41
374-42	Cellophane Avisco	17,330	23	2,430	29
79	HEPVA	5,900	583	2,210	785
374-59	HEPVA High m.wt.	4,330	660	1,920	830
374-60	HEPVA Med. m.wt.	4,950	590	1,860	735
374-61	Polyvinyl Alcohol (commercial)	9,660	435	6,070	705
389-93	Polyvinyl Alcohol (30-98)	9,150	155	3,620	528
389-105	Methocel 15	10,100	3	6,340	18
389-104	Methocel 100	8,250	5	6,980	29
389-103	Methocel 400	11,000	5	7,640	26
407-34-1	Methyl Cellulose Modification D	5,920	23	4,370	25
407-34-2	Methyl Cellulose Modification A	4,950	9	3,205	17
407-34-3	Methyl Cellulose Modification B	8,660	7	4,107	24
407-34-4	Methyl Cellulose Modification C	8,830	5	5,497	25

Table XI - Design Parameters Common to Ag_2O-Zn Cells SS 5.5 at Burgess

Design Parameters	
No. of Ag_2O Plates	6
No. of Zn Plates	7
Wt. Ag_2O/Plate	6.9 gm. (1.60 A.H.)
Wt. Zn/Plate	3.2 gm. (2.64 A.H.)
Ag_2O Plate Size	1.75 x 2.125 x 0.028 in.
Zn Plate Size	1.75 x 2.125 x 0.030 in.
Theoretical Cathode Ag_2O Capacity	9.65 A.H.
Theoretical Anode Capacity	18.45 A.H.
Separator	Single layer per plate side, 0.002 in. Aldex No. 13

Table XII - Summary of Cell Cycling Tests at Burgess (Ag_2O-Zn Cells SS 5.5 with Design Parameters as Summarized in Table XI).

Diaphragm Material	PUDO Cellophane 193	Borden PVAlc 78	Borden HEPVA 79
Burgess Construction Type:	IV	V	VI
Film Thickness (inches)	0.001	0.003	0.002
Layers per plate side	5	2	3
Figures showing typical discharge voltage curves	No. 6	No. 8	No. 10
Figure showing cycle life data	No. 7	No. 9	No. 11
Number of cycles after which cycling regime was terminated	still going at 17 cycles	17	9
Reason for termination	-	at 17th cycle delivered less than 60% of theoretical Ag_2O capacity	on 9th cycle failed by short through diaphragm

Table XIII - Cycling Data

Cycle	Discharge Rate Amp.	Construction Type IV DuPont Cellophane Discharge Time Hr.	Construction Type IV DuPont Cellophane Discharge Output A.H.	Construction Type V Borden PVAlc Discharge Time Hr.	Construction Type V Borden PVAlc Discharge Output A.H.	Construction Type VI Borden HEPVA Discharge Time Hr.	Construction Type VI Borden HEPVA Discharge Output A.H.
1	2	5.41	10.82	4.15	8.30	4.47	8.94
2	2	5.60	11.20	4.77	9.54	5.22	10.44
3	10	1.08	10.80	.42	4.20	1.08	10.80
4	50	.17	8.50	.02	1.00	.10	5.00
5	2	6.82	13.64	6.40	12.80	7.03	14.06
6	2	5.71	11.42	5.25	10.50	6.22	12.44
7	2	6.05	12.10	5.15	10.30	6.15	12.30
8	2	5.67	11.34	4.78	9.56	6.02	12.04
9	2	5.36	10.72	4.58	9.16	.00	.00
10	2	5.00	10.00	4.85	9.70		
11	2	5.10	10.20	3.38	6.76		
12	2	4.91	9.82	3.82	7.64		
13	2	4.52	9.04	3.98	7.96		
14	2	4.38	8.76	3.30	6.60		
15	2	4.36	8.72	3.15	6.30		
16	2	4.15	8.30	3.52	7.04		
17	2	3.68	7.36	2.87	5.74		

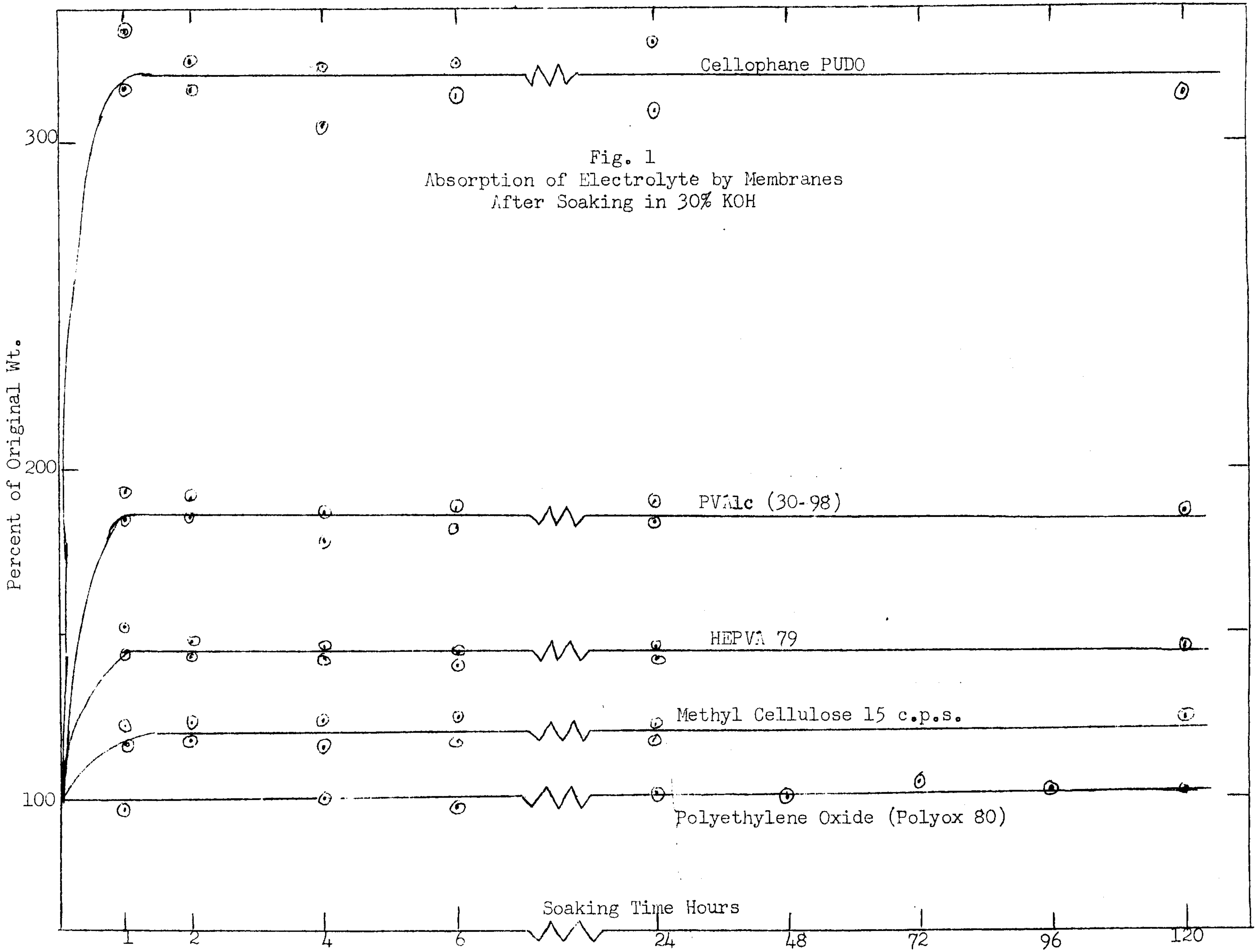


Fig. 1
Absorption of Electrolyte by Membranes
After Soaking in 30% KOH

Fig. 2
Absorption of Electrolyte by Membranes
After Soaking in 40% KOH

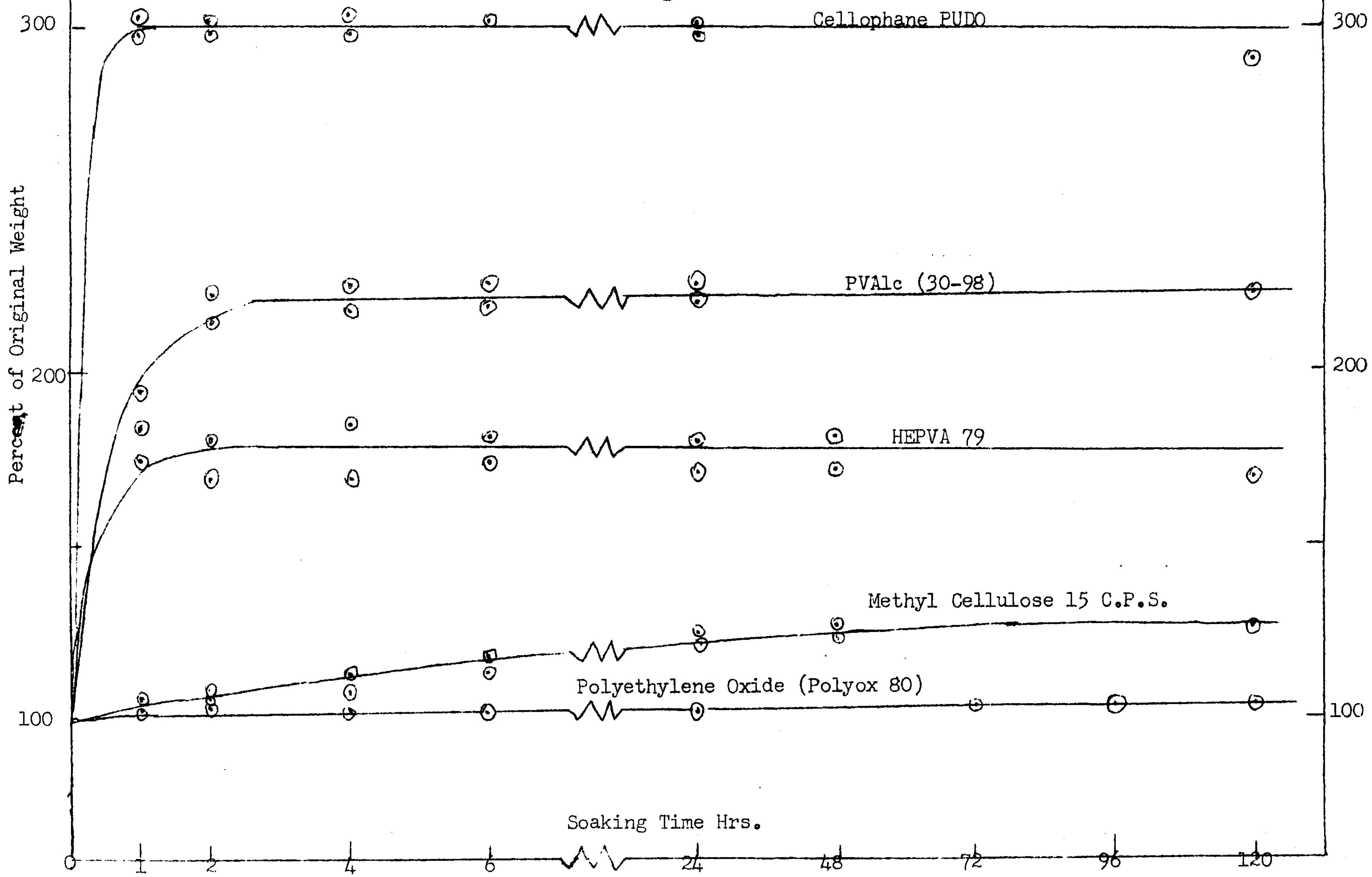


Figure 3 - Absorption of Electrolyte by Membranes After Soaking in 30% KOH

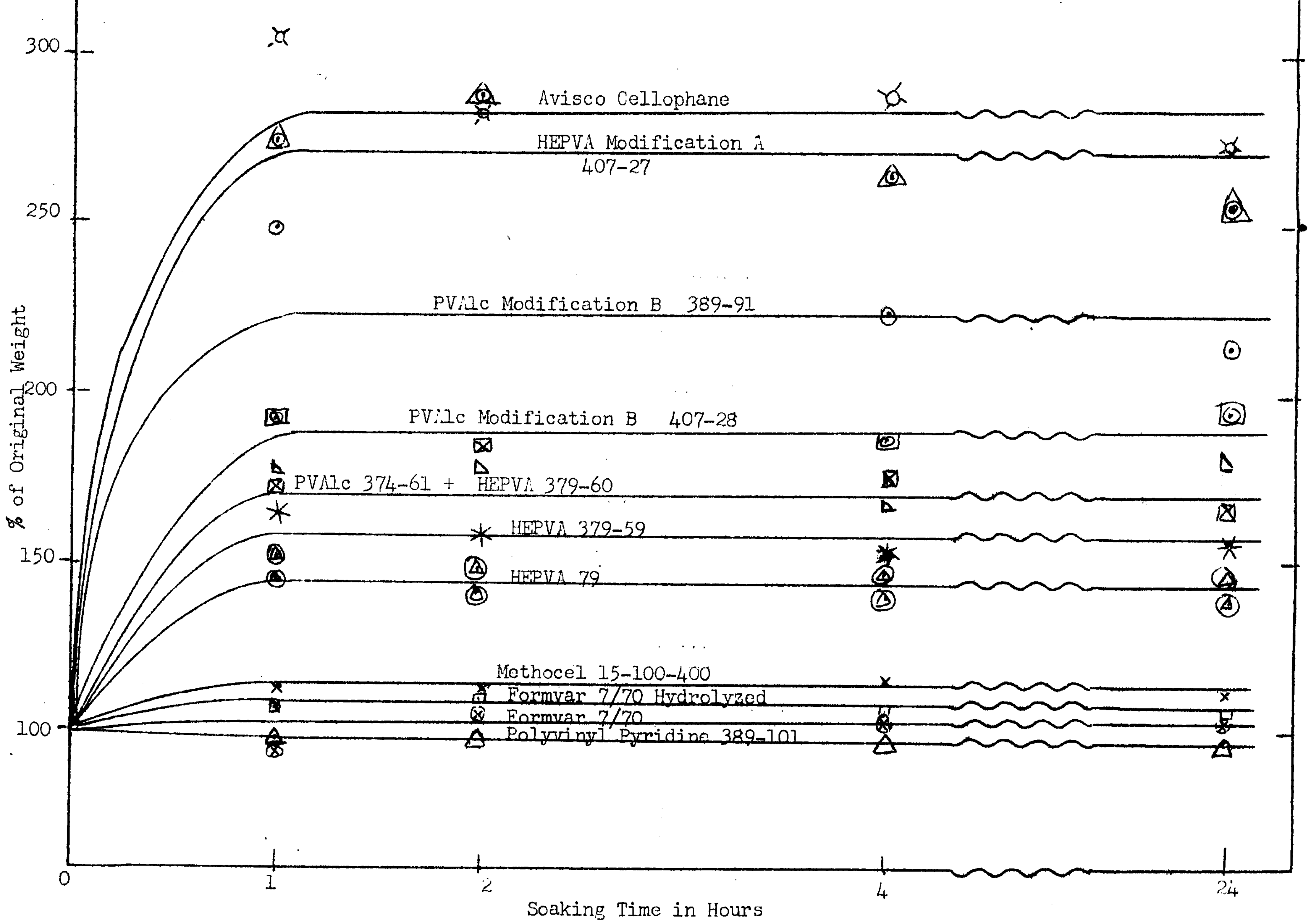
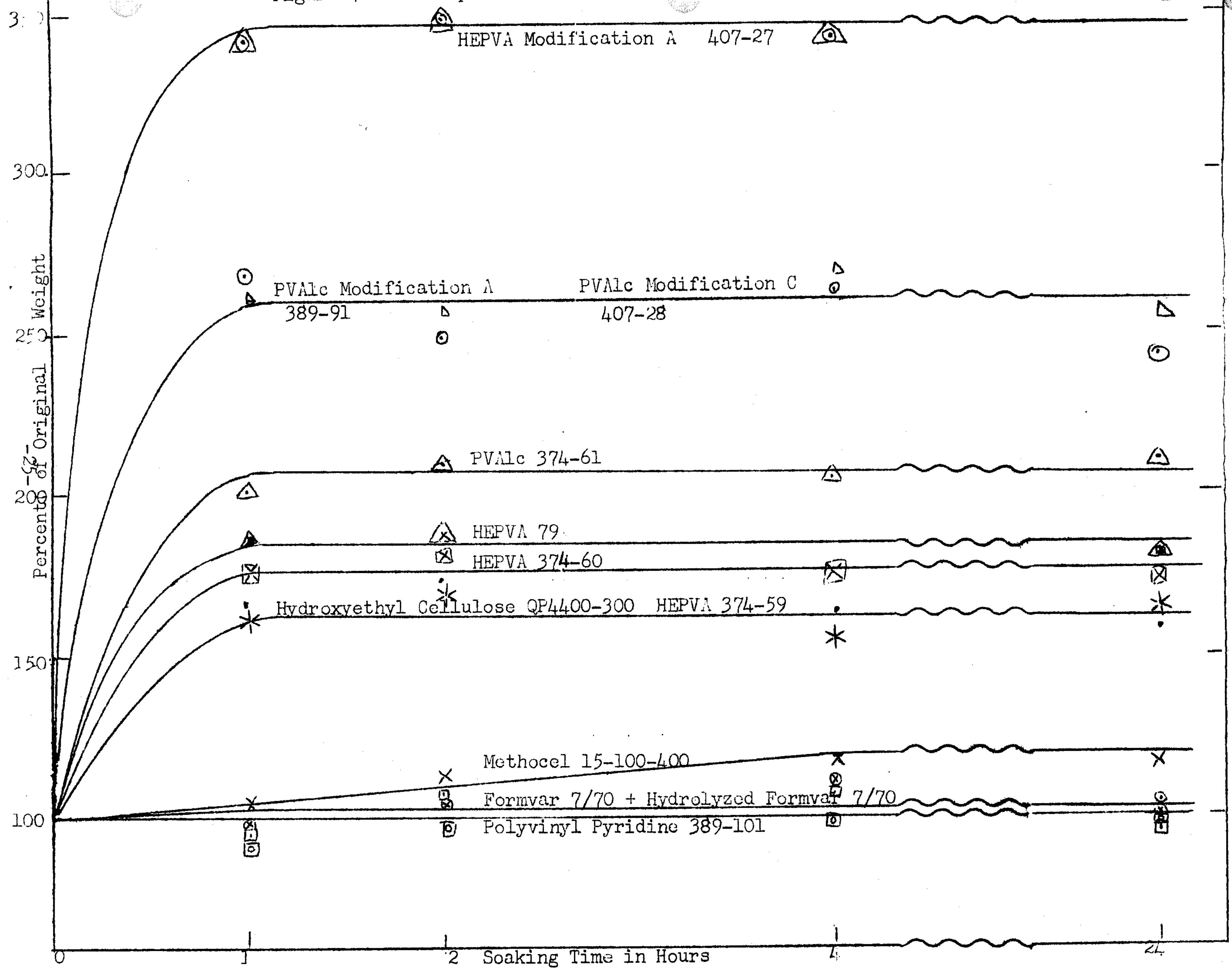


Figure 4 - Absorption of Electrolyte by Membranes After Soaking in 40% KOH



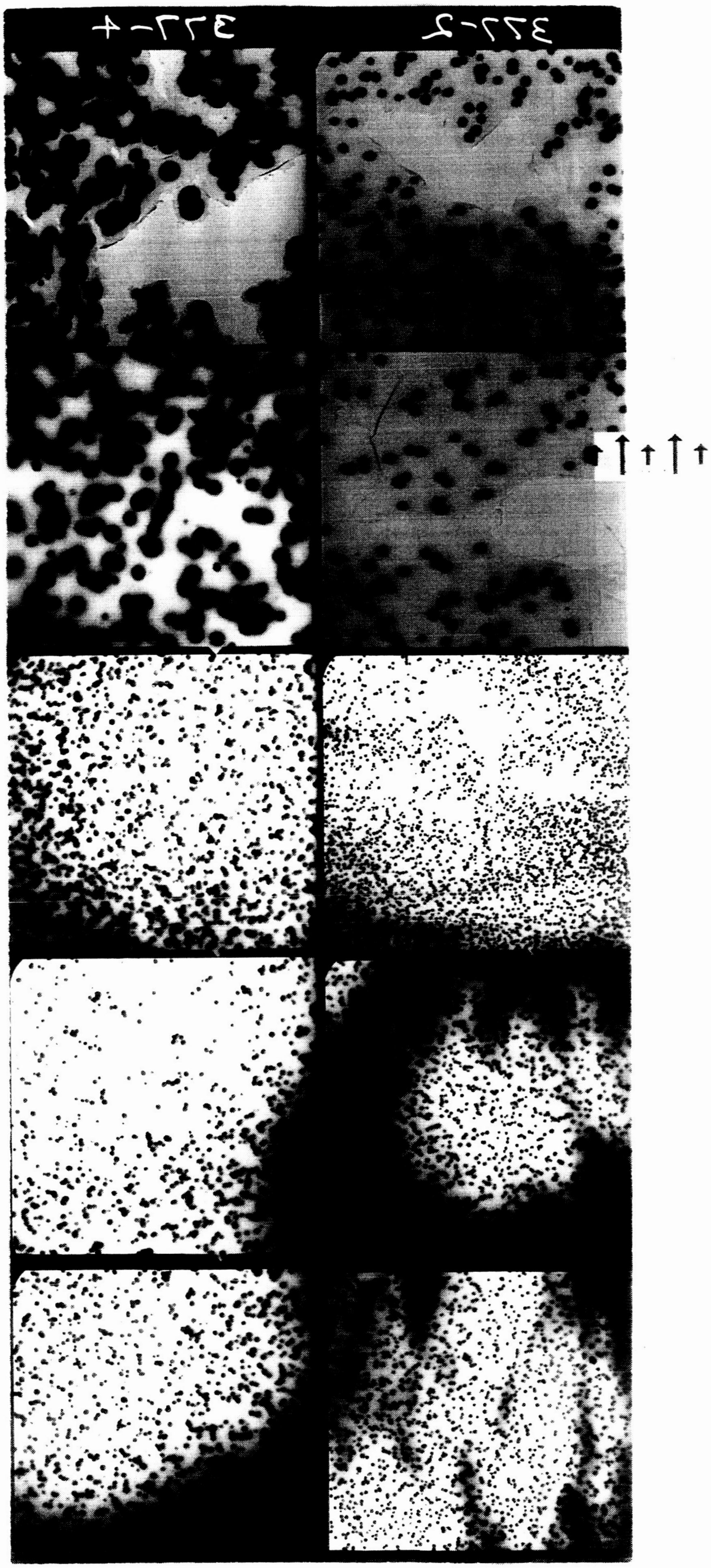


Fig. 5 - Polyox 80 Film
Electron Micrograph

Magnification - 8.5 mm = 1 u
(Note rupture of film by
Electron beam)

Magnification - 2.66 mm = 1 u

Fig. 6

Construction Type IV, Typical Dischg. Curves

Cellophane PUDO 193

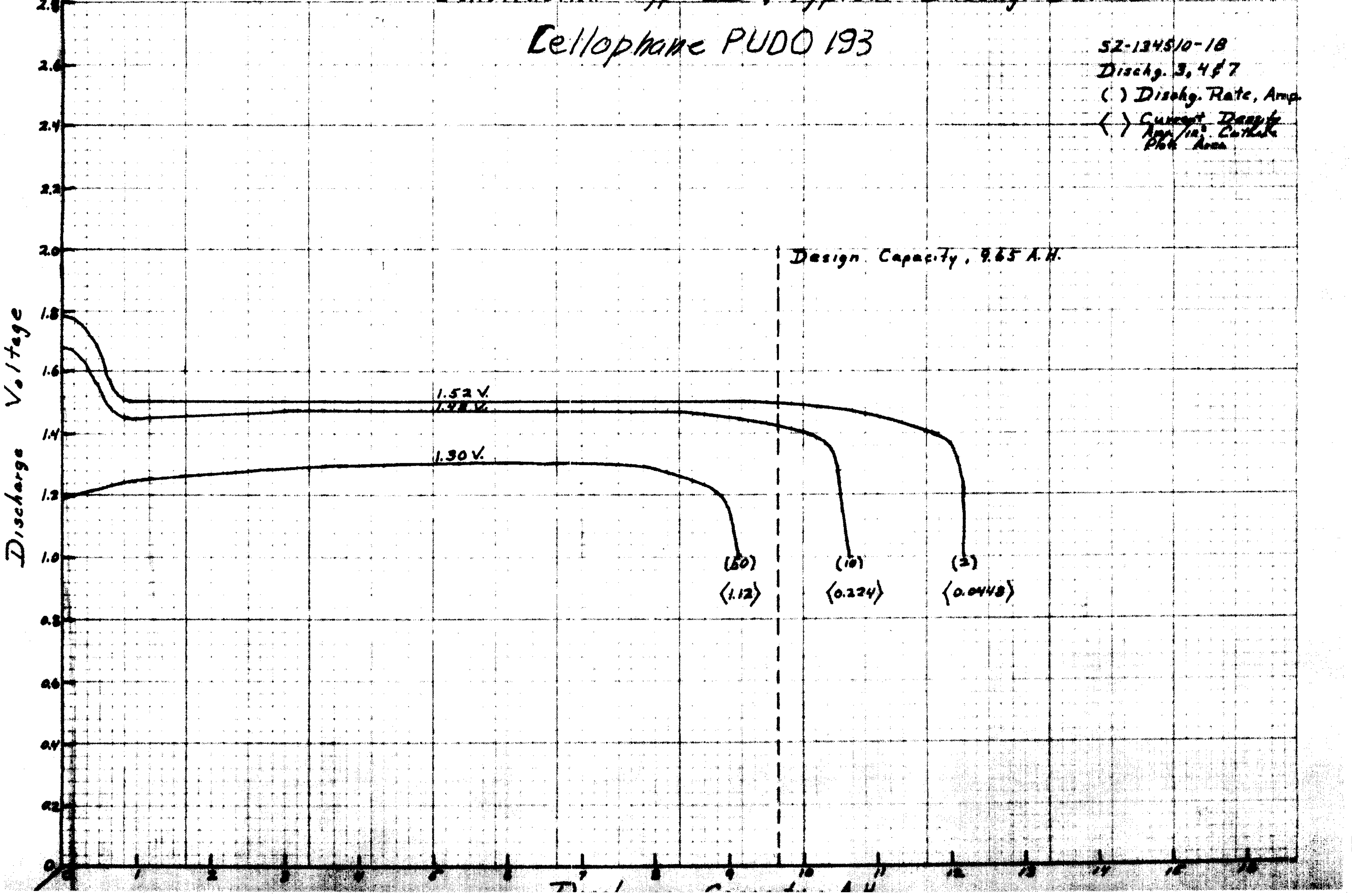
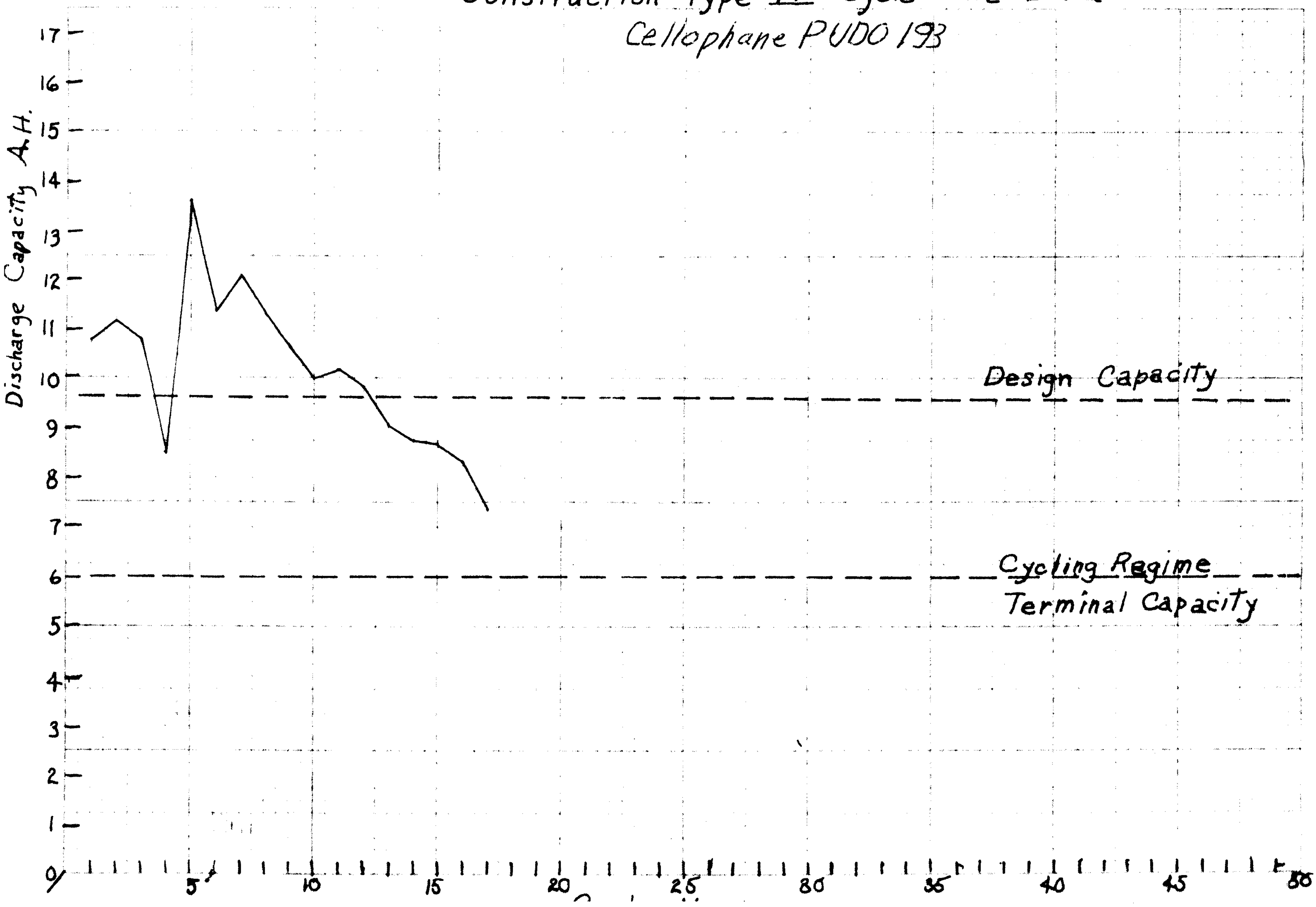


Fig. 7

Construction Type IV Cycle Life Data

Cellophane PUDO 193



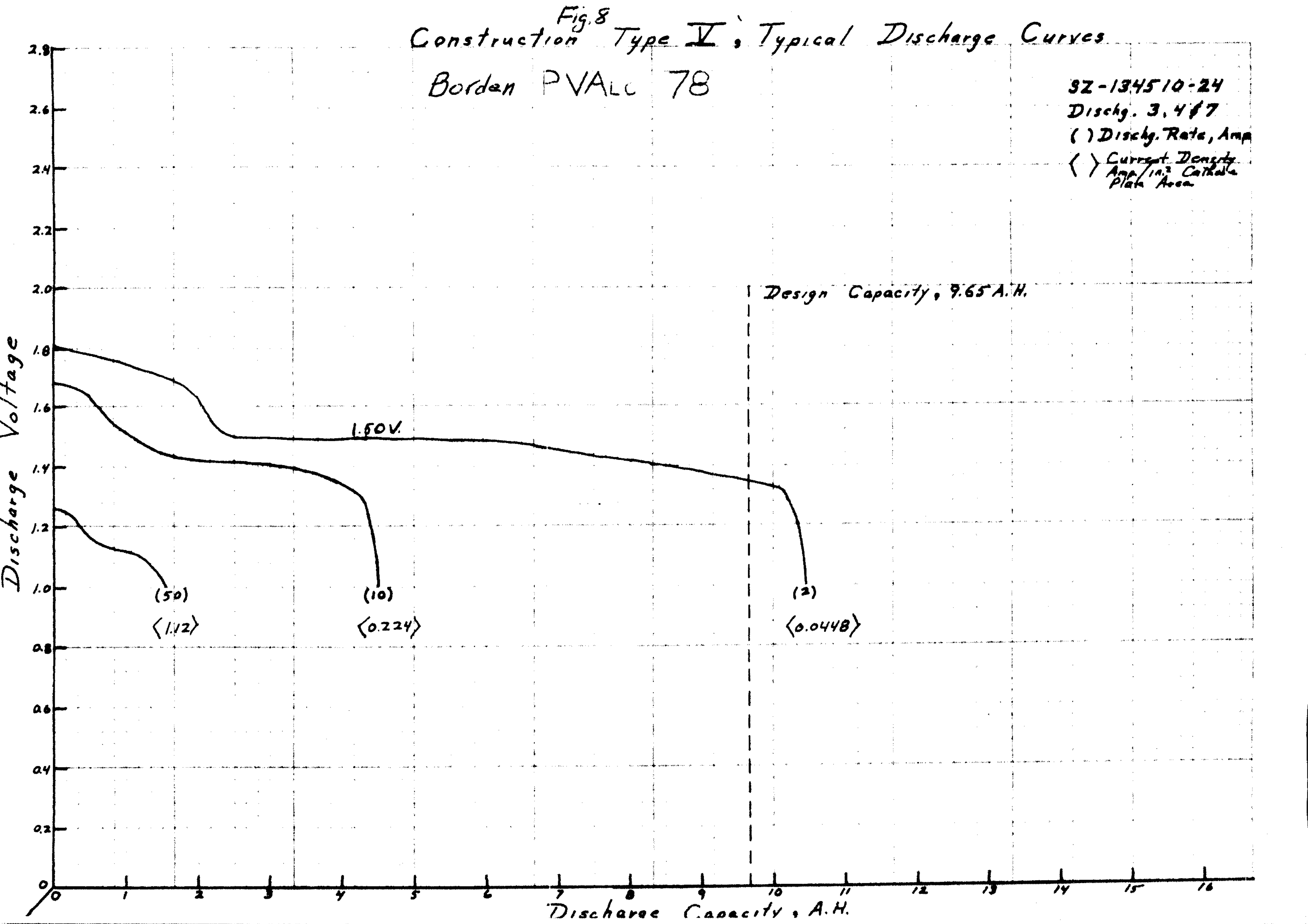


Fig. 8
Construction Type V; Typical Discharge Curves
Borden PVAlc 78
3Z-134510-24
Dischg. 3, 4 & 7
( ) Dischg. Rate, Amp
⟨ ⟩ Current Density Amp/in.² Cathode Plate Area
Design Capacity, 9.65 A.H.
1.50V.
(50)
⟨1.12⟩
(10)
⟨0.224⟩
(2)
⟨0.0448⟩
Discharge Voltage
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Discharge Capacity, A.H.

Fig. 9
Construction Type V Cycle Life Data
Borden PVALC 78

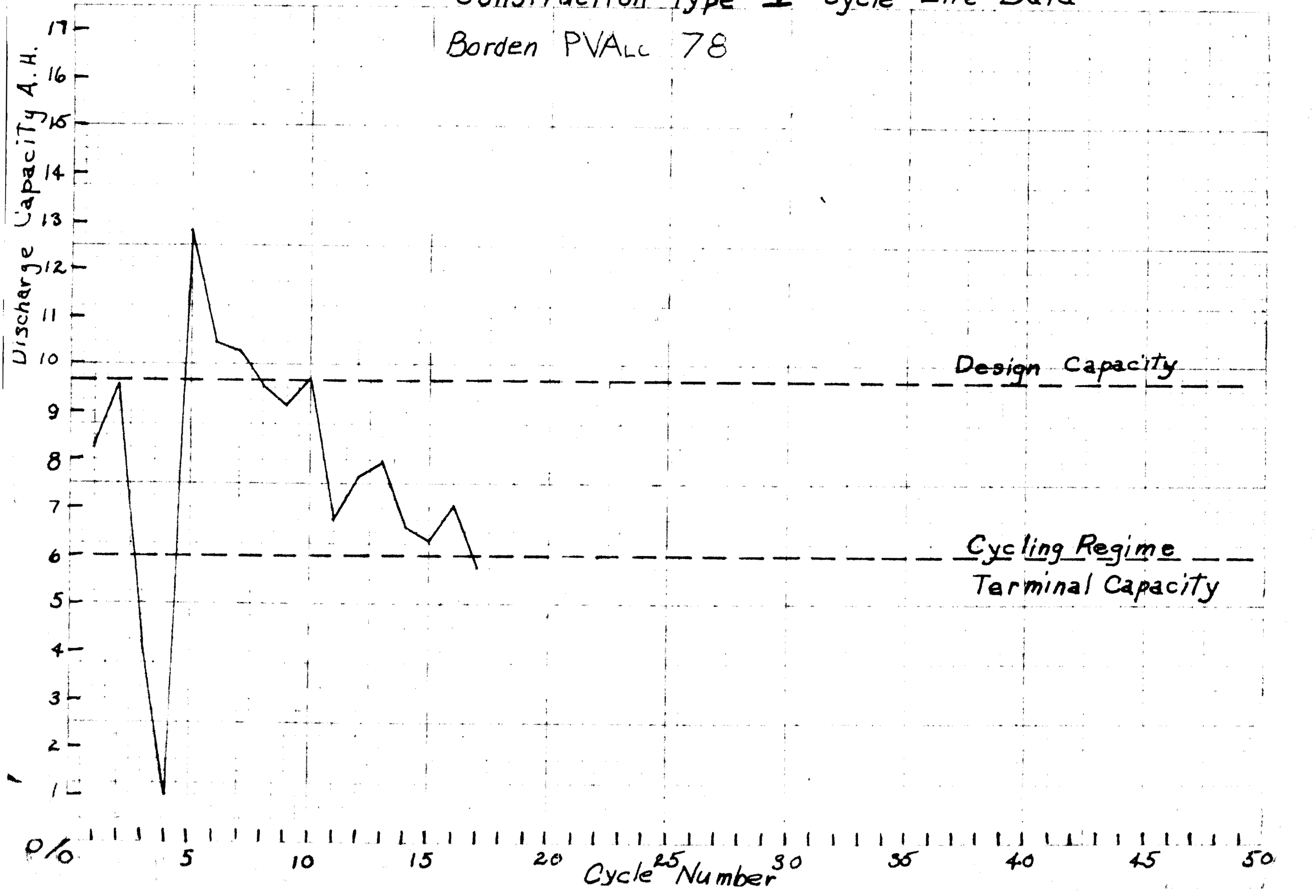


Fig. 10

Construction Type VII, Typical Dischg. Curves

Borden HEPVA 79

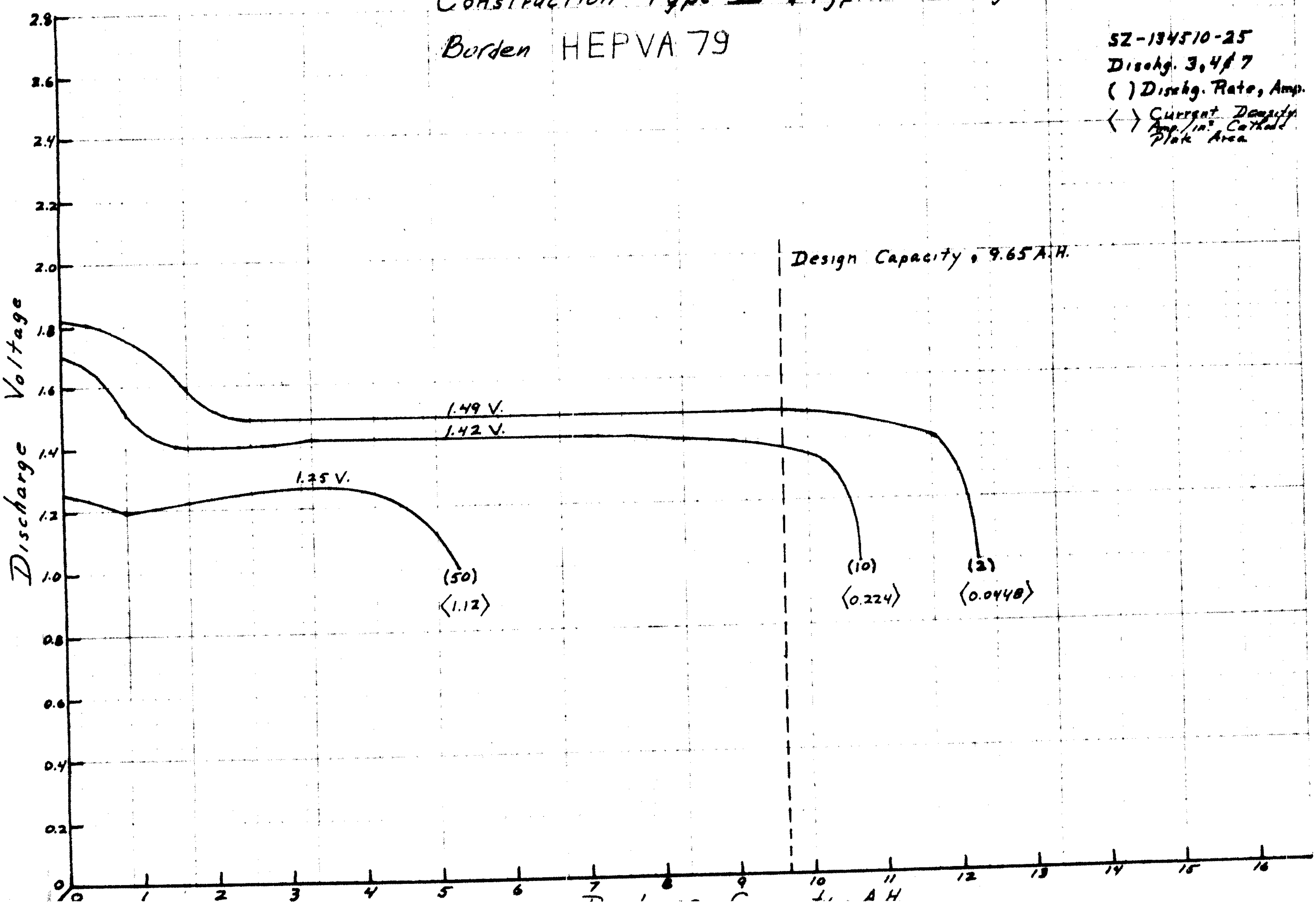
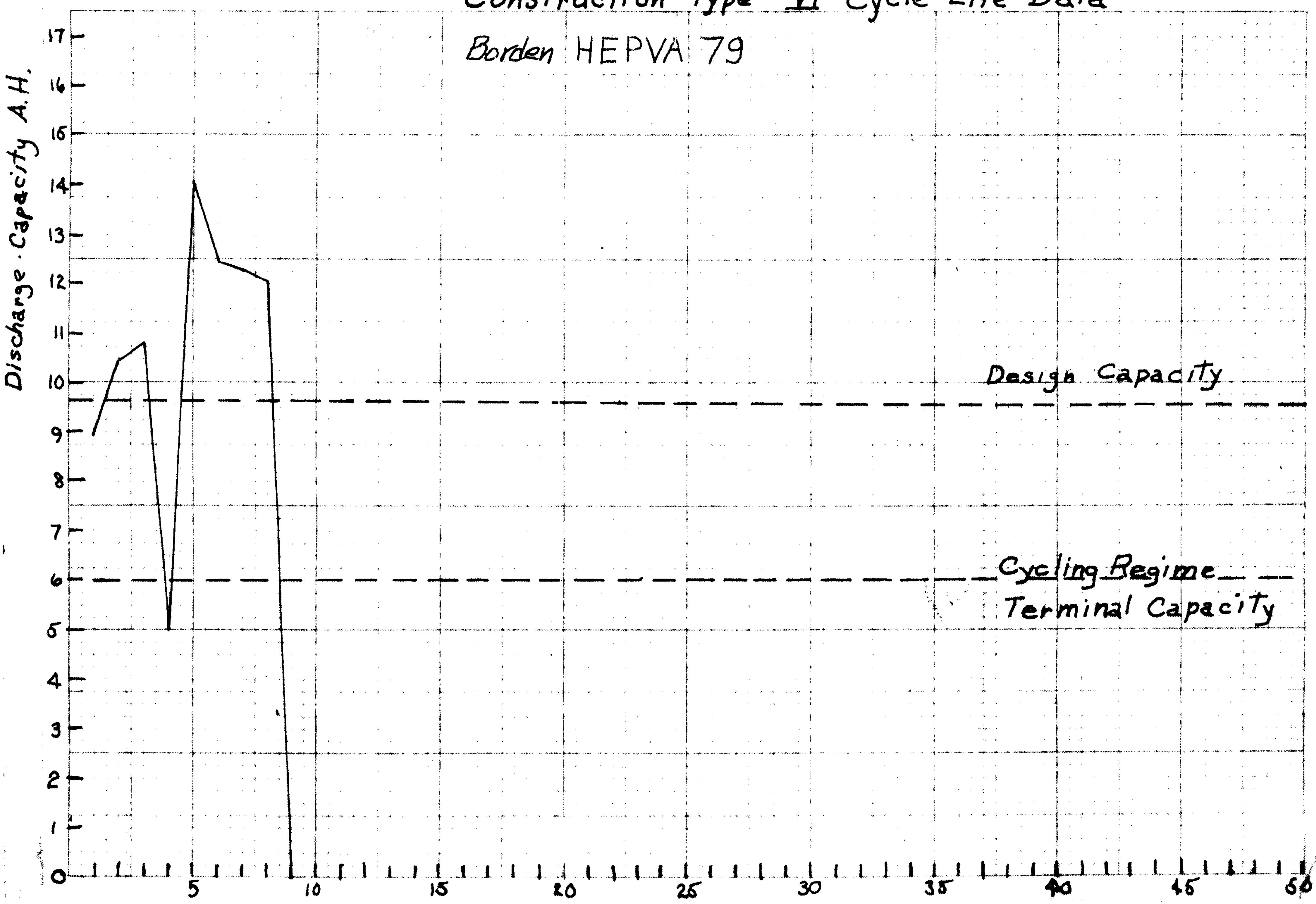


Fig. 11

Construction Type VI Cycle Life Data

Borden HEPVA 79



ERRATA

First Quarterly Report
June 27, 1963 - Sept. 27, 1963
Contract No. NAS 5-3467

p. 12	para. 2	line 7	change "the"	to	"to"	
p. 12	Table II	Under KOH 40%	Hydroxyethyl Cellulose "insol."			
p. 14	para. 4	line 4	change "carboxyl"	to	"carbonyl".	
p. 22		line 4	change "30%"	to	"<90%"	
p. 22		line 5	change "(rate not stated)"	to	"(25 G for 2 min.)"	